

UNITED STATES PATENT APPLICATION FOR:

METHOD FOR DETERMINING A CONCENTRATION OF CONDUCTIVE  
SPECIES IN AN AQUEOUS SYSTEM

INVENTORS:

DEENESH PADHI  
SRINIVAS GANDIKOTA  
CHRIS MCGUIRK  
GIRISH DIXIT

ATTORNEY DOCKET NO.: AMAT/5933/CALB/COPPER/PJS

CERTIFICATION OF MAILING UNDER 37 C.F.R. 1.10

I hereby certify that this New Application and the documents referred to as enclosed therein are being deposited with the United States Postal Service on 1-8-02, in an envelope marked as "Express Mail United States Postal Service", Mailing Label No. EV041916131US, addressed to: Assistant Commissioner for Patents, Box PATENT APPLICATION, Washington, D.C. 20231.

  
Signature

BETH MULCAHY  
Name

1-8-02  
Date of signature

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

**METHOD FOR DETERMINING A CONCENTRATION OF CONDUCTIVE  
SPECIES IN AN AQUEOUS SYSTEM**

**BACKGROUND OF THE INVENTION**

**Field of the Invention**

[0001] The invention relates to a method for determining a concentration of conductive species in an aqueous system.

**Description of the Background Art**

[0002] An aqueous system typically comprises a solution of one or more ionic (electrically conductive) or nonionic (typically non-conductive) chemical species in water. Because water is such a ubiquitous substance, aqueous systems are present throughout nature and are utilized frequently for industrial processes in the manufacture of durable and nondurable goods. Often it is desirable to characterize the chemical properties of the aqueous system at various points in time, for example, to determine the integrity of the system, or to determine how the system may respond to various external stimuli, etc. In particular, it is often desirable to measure the concentration of one or more chemical species in the aqueous system to provide an indication of the system's properties.

[0003] Methods for determining the concentration of chemical species in an aqueous system are widespread and numerous, some of which methods are capable of measuring the concentration of electrically conductive species. Such methods include those employing instrumentation such as mass spectrometry, gas chromatography, ultraviolet-visible spectrophotometry, etc. Other methods employ so called "wet chemical" techniques and consist essentially of sampling the aqueous system and subjecting the sample to one or more chemical reactions, separations, or similar processes.

[0004] In the case of many aqueous systems, it is undesirable to use instrumental or wet chemical methods to determine the concentration of chemical species in the aqueous system. Instrumental methods are typically very expensive in terms of the cost to provide and service the instrumentation. On the other hand, wet chemical methods tend to be labor intensive, time consuming, and somewhat inaccurate.

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

**[0005]** Wet chemical techniques are frequently employed to determine, for example, the concentration of acid present in an electrochemical plating bath. Determination of the concentration of acid is important for this application, as the acid concentration greatly influences the performance and throughput of the electrochemical plating operation. To carry out a wet chemical technique, samples of the electrochemical plating bath are removed from the bath at particular time intervals, and a wet chemical assay, such as a titration operation, is performed to determine acid concentration.

**[0006]** A typical titration operation involves at least half a dozen individual titrations in order to arrive at a precise value of acid concentration. This operation may require as long as an hour or more to perform, and involves an inventory of multiple chemical reagents and various pieces of hardware that must be cleaned and maintained for use in subsequent assays.

**[0007]** In order to circumnavigate the above-identified problems involving instrumentation and wet chemistry, other methods attempt to measure a parameter that can be related to electrolyte concentration rather than directly measuring the concentration. For example, a conductivity or pH meter can be used to measure conductivity of a sample, and this can be related to the activity or concentration of hydrogen ions in an aqueous system. Unfortunately, this method is not appropriate to many systems, particularly those systems that have very high concentrations of acid or alkali. Conductivity meters and pH meters also tend to be relatively insensitive to small fluctuations in acid or alkali concentration that may be of significant interest to one monitoring the aqueous system.

**[0008]** Electrochemical plating baths used for copper plating in the production of semiconductor wafers present a problem in measurement and control of the concentration of both organic and inorganic species present as additives to catalyze different aspects of plating. While organics are added to improve the gap-fill performance, the inorganics play an important role in tailoring the conductivity of the bath as well as in enhancing the activity of the organics. Measurement and control of the concentration of these species are crucial to obtaining reliable gap-fill in sub-micron features. Ideal operation would include accurate and continuous real-time monitoring and control.

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

[0009] In the copper plating of semiconductor wafers, the wafer and the anode (typically a copper disk) are immersed in an electrolyte containing a copper salt, most commonly copper sulfate. When the wafer is biased negatively and the anode biased positively, copper is deposited on the wafer. The electrolyte also usually contains a strong acid, such as sulfuric acid, to increase the conductivity of the plating bath and thereby increase the current carrying capability of the solution and the rate of deposition of copper. In order to control the amount of copper deposited, it is necessary to know the acid concentration in real time, so the concentration can be controlled by increasing or decreasing the rate of addition of the acid. Such real-time monitoring and control has not heretofore been possible by available methods and apparatus.

[0010] Therefore, a need exists for an improved method for determining concentrations of electrolytes in an aqueous system, such as an electrolytic bath for copper plating of semiconductor wafers.

**SUMMARY OF THE INVENTION**

[0011] One or more embodiments of the present invention provides a method of determining concentrations of conductive species in an aqueous system. In one embodiment, the method comprises providing an electrochemical cell having a cell resistance that varies with a concentration of conductive species and determining a relationship between the cell resistance and the concentration of conductive species. The method further comprises measuring one or more electrochemical parameters of the electrochemical cell and determining a test concentration of conductive species based upon the one or more measured electrochemical parameters.

[0012] In at least one embodiment of the invention, the relationship between cell resistance and the concentration of conductive species is determined by providing a first concentration of conductive species and measuring at least one electrochemical parameter, such as cell voltage or cell current, of the electrochemical cell. The concentration of conductive species is then adjusted to provide a second concentration of conductive species substantially different than

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

the first concentration of conductive species and at least one electrochemical parameter of the electrochemical cell is measured.

**[0013]** Also provided is a method of determining whether an aqueous system has a concentration of conductive species that falls within a specified range. The method comprises providing an electrochemical cell wherein the electrochemical cell has a cell resistance that varies with a concentration of conductive species and determining a relationship between the cell resistance of the electrochemical cell and the concentration of conductive species. The method further comprises measuring one or more electrochemical parameters of the electrochemical cell and determining a test concentration of conductive species based upon the one or more measured electrochemical parameters. If the test concentration is less than a pre-determined maximum concentration and more than a predetermined minimum concentration, then it is concluded that the concentration falls within the specified range.

**[0014]** Also provided is a method for continuously measuring the concentration of conductive species in an electrochemical plating bath, thereby providing a continuous real-time analysis and allowing constant adjustment of the addition of conductive species to the plating bath, as required to maintain a desired concentration. The method comprises the steps of providing an electrochemical plating bath comprising an electrolyte with conductive species therein and further providing an anode and a cathode. The anode, cathode, wiring, connections and the electrochemical plating bath define an electrochemical cell wherein the electrochemical cell has a cell resistance that varies with a concentration of conductive species. The method further comprises determining a relationship between the cell resistance of the electrochemical cell and the concentration of conductive species by measuring one or more electrochemical parameters of the electrochemical cell, and determining a test concentration of conductive species based upon the one or more measured electrochemical parameters.

**[0015]** Furthermore, a system for electroplating a material layer on a substrate is provided. The system comprises an electroplating apparatus for electroplating a material layer on a substrate. The electroplating apparatus comprises an electrochemical cell, including an electroplating bath. The system further

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS

Express Mail No. EV041916131US

comprises a sensing device capable of measuring cell resistance and one or more material storage reservoirs capable of delivering one or more materials to the electrochemical plating bath at a rate in response to the measurements, in order to continuously adjust the concentration of conductive species therein on a real-time basis.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0016] FIG. 1 is a schematic illustration of an aqueous system comprising conductive species, the concentration of which may be measured using the embodiments described herein;

[0017] FIG. 2 depicts a graphical relationship between cell resistance and concentration of conductive species in an aqueous system;

[0018] FIG. 3 is a process flow diagram depicting a method for determining the concentration of an aqueous system in accordance with one or more embodiments of the invention described herein;

[0019] FIG. 4 is a cross sectional view of an electrochemical plating process cell that may be used to practice one or more embodiments described herein; and

[0020] FIG. 5 is a cross-sectional schematic representation of electrochemical plating cell and associated electrical circuitry.

**DETAILED DESCRIPTION OF THE INVENTION**

[0021] One or more embodiments of the present invention provide a method of measuring a concentration of conductive species in an aqueous system. FIG. 1 is a schematic illustration of an aqueous system comprising an electrolyte 100. Electrolyte 100 may be, for example, an electrochemical plating bath or an electroplating bath (note the term electrochemical plating and the term electroplating are used interchangeably throughout this discussion).

[0022] In order to measure concentrations of conductive species in electrolyte 100, an electrochemical cell 102 is provided. Electrochemical cell 102 typically comprises an anode 104 and a cathode 106 which serve as electrodes in the electrochemical cell 102. The electrochemical cell 102 further comprises an electrochemical sensing device 108. Electrochemical sensing device 108 is

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS

Express Mail No. EV041916131US

coupled to anode 104 and to cathode 106 by electrically conductive leads 110. As shown in FIG. 1, the electrolyte 100, the anode 104, the cathode 106, the electrochemical sensing device 108, and the conductive leads 110 define the electrochemical cell 102. In one embodiment, the cathode 106 has a cross-sectional area and the anode 104 has a cross-sectional area, and the cross-sectional area of the anode 104 and the cross-sectional area of the cathode 106 are about the same in magnitude. For example, cross-sectional area of the anode 104 may be within a range of about 85% to about 115% of the cross-sectional area of the cathode 106.

**[0023]** Electrolyte 100 has a composition that is variable, but generally comprises water and conductive species. The conductive species are ionized, and are capable of significant and directional mobility in response to a voltage applied across the anode 104 and the cathode 106. The conductive species may comprise, for example, hydrogen ions, hydroxyl ions, metal ions, inorganic or organic salts, and combinations thereof. While it is advantageous that the conductive species are predominantly comprised of one particular chemical moiety (for example, hydrogen ions), it is within the scope of the invention for the conductive species to comprise a number of dissimilar chemical moieties.

**[0024]** While it is advantageous that the conductive species are predominantly comprised of one particular chemical moiety (for example, hydrogen ions), it is within the scope of the invention for the conductive species to comprise a number of dissimilar multiple chemical moieties. Electrolyte 100 may further comprise nonconductive species that are substantially incapable of significant and directional mobility through electrolyte 100 under influence of a voltage applied across the anode 104 and the cathode 106. Such nonconductive species may include, for example, organic moieties, unionized or insoluble salts, etc. Thus, for example, electrolyte 100 may comprise one or more acids, alkalis, or salts as well as organic polymers, surface-active agents, etc.

**[0025]** The electrochemical sensing device 108 comprises circuitry (not shown) that enables it to sense electrochemical parameters associated with the electrochemical cell 102. In particular, in one embodiment, device 108 is capable of applying a fixed voltage,  $V$ , to the electrochemical cell 102, and then sensing a

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

cell current,  $I$ , that travels through electrochemical cell 102. Alternatively, device 108 may be capable of applying a fixed cell current to the electrochemical cell 102, and then sensing a cell voltage,  $V$ , that develops across the electrochemical cell 102. The sensing device 108 may comprise, for example, one or more current sources, one or more voltage sources, a voltage meter, a current meter, and combinations thereof. Many methods that are well known to those of ordinary skill the art exist for fabricating current sources, voltage sources, voltage meters, and current meters that are suitable for fabricating embodiments of the sensing device 108.

**[0026]** By sensing the cell current,  $I$ , travelling through the electrochemical cell 102 in response to an applied voltage,  $V$ , or by sensing the cell voltage that develops across the electrochemical cell 102 in response to an applied cell current, the sensing device 108 is capable of determining the cell resistance,  $R$ , given by the Ohm's law relationship,  $R = V / I$ . The cell resistance is the total electrical resistance of the electrochemical cell, defined by the ratio of the voltage drop across the electrochemical cell 102 to the cell current travelling through the electrochemical cell 102.

**[0027]** The cell resistance is dependent upon the composition of the electrolyte 100, and in particular, the cell resistance is dependent upon the nature and concentration of conductive species therein. The cell resistance is also dependent upon thermodynamic variables, such as temperature of the electrolyte 100, process variables, such as the flow rate of the electrolyte 100, as well as the geometry of the electrochemical cell 102. Geometric parameters that influence the cell resistance include the cross sectional area of the anode 104 and the cathode 106 as well as the distance between the anode 104 and the cathode 106.

**[0028]** The inventors have found that if the temperature of the electrolyte 100, the flow rate of the electrolyte 100, the nature of the conductive species, and the electrode geometry are held constant, variation in other factors has negligible effect, and the cell resistance,  $R$ , is directly related to the concentration of conductive species. In fact, the relationship between the two variables is often linear as shown in FIG 2. The linear relationship between cell resistance and



**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

concentration of conductive species is often realized across a wide range of concentration of conductive species.

**METHOD OF MEASURING CONCENTRATION OF CONDUCTIVE SPECIES**

[0029] In order to determine a concentration of conductive species in an aqueous solution, one may take advantage of the relationship between cell resistance and the concentration of conductive species as described above.

[0030] In particular, to determine the concentration of conductive species, one first determines a relationship between the cell resistance of the electrochemical cell 102 and the concentration of conductive species. The measurement process is depicted in the process flow diagram of FIG. 3. The process begins with step 300. The relationship between cell resistance and concentration of conductive species is determined by providing an electrolyte having a first concentration of conductive species therein, as shown in step 302. The first concentration of conductive species is a known quantity because the quantity of conductive species has been measured before adding the conductive species to the electrolyte within the electrochemical cell 102. It is further assumed that the conductive species added to the electrolyte ionize completely.

[0031] At least one electrochemical parameter is then measured, as shown in step 304 using sensing device 108. In a preferred embodiment, a cell current is applied to the electrochemical cell 102, and the cell voltage developed across the anode 104 and the cathode 106 is measured. The cell current and cell voltage are used to calculate the cell resistance through the Ohm's law relationship described above. In a preferred embodiment, the applied cell current is a direct (DC) current. While the preceding discussion as well as the discussion that follows provides for applying a fixed cell current and sensing a voltage, alternatively a fixed voltage may be applied and a cell current traveling through electrochemical cell 102 is measured.

[0032] After measuring the cell voltage, the concentration of conductive species is then adjusted to form a second concentration of conductive species, as depicted in step 306. This may be accomplished, for example, by adding a known mass or concentration of conductive species to the aqueous system. It is

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS

Express Mail No. EV041916131US

preferred that the second concentration of conductive species be substantially different from the first concentration of conductive species. In that case, the second concentration and the first concentration advantageously define a range of concentration values that is likely to encompass the concentration of conductive species in electrolyte 100 throughout a span of time. The span of time is that period during which measurements of concentration are desired for electrolyte 100.

[0033] Alternatively, it is within the scope of the invention to adjust the concentration through other means, such as, for example, by adding a known quantity or concentration of a chemical species that reacts with the conductive species and reduces the concentration of conductive species in a predictable way.

[0034] After adjusting the concentration of conductive species, a fixed cell current is applied to the electrochemical cell 102, and cell voltage is remeasured, according to step 308. As indicated previously, it is desirable to keep constant variables such as temperature, flow rate, etc. that may influence the electrochemical parameters. For example, the temperature of the electrochemical cell 102 may be held at a first temperature. Furthermore, it is further preferred that the cell current applied in step 308 has a magnitude that is substantially similar to the cell current that is applied in step 304.

[0035] Step 306 of adjusting the concentration of conductive species and step 308 of measuring electrochemical parameters may be repeated one or more times, as shown in path A of Fig. 3, to provide increasing detail and confidence concerning the relationship between concentration of electrolyte and cell resistance. Each time the concentration of electrolyte is adjusted, cell voltage is determined and cell resistance is calculated. In a preferred embodiment, the additional concentrations of conductive species are substantially different from one another and from the first concentration of conductive species and the second concentration of conductive species. As indicated previously it is preferred that throughout the process of adjusting concentration and measuring cell voltage, various process parameters are held substantially constant. It is further preferred that the applied cell current be maintained substantially constant from one cell voltage reading to the next.

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

**[0036]** Through the above-described sequence of adjustments in concentration of conductive species and electrochemical parameters, a relationship between concentration of conductive species and the cell resistance is developed and can be used to determine the concentration of conductive species at a future point in time. The relationship may be expressed in the form of a graph, such as the graph shown in FIG. 2.

**[0037]** It is within the scope of the invention to generate a plurality of relationships such as the one described in FIG. 2 for various conditions to which the electrochemical cell is exposed. Referring again to FIG. 3, if it were desirable to know the concentration of electrolyte within the electrochemical cell 102 within a range of a particular process value (such as, for example, within a range of electrochemical cell temperatures) one would adjust the process value, in this example, the temperature, as shown in step 309 to a second temperature substantially different than the first temperature. Steps 302 to 308 are then repeated, conducting the measurements of cell voltage at the second temperature. In this manner a second relationship between cell resistance and concentration of electrolyte is determined. Path B, of FIG. 309 illustrates this process. Movement along path B may be repeated in order to develop a relationship between cell resistance and concentration for a series of temperatures.

**[0038]** In another embodiment of the present invention, one determines a series of relationships between cell resistance and concentration while adjusting a second process variable. The second process variable may be, for example, cell current. It is therefore conceivable that upon completing step 310, one may determine a relationship between cell resistance and concentration for a range of a first process variable (e.g. for a range of cell temperatures), a relationship between cell resistance and concentration for a series of a second process variable (e.g. cell current), as well as for additional process variables, such as the spacing of the cathode and anode, other electrode geometry, the flow rate of the electrolyte, and the nature of the conductive species.

**[0039]** Referring again to FIG. 3, at step 312, at a point in time in which knowledge concerning the concentration of conductive species is desired, once

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS

Express Mail No. EV041916131US

again, an electrochemical parameter such as cell voltage is measured as described previously in order to determine cell resistance. The measurements are preferably performed under process conditions similar to those used to determine the one or more relationships between cell resistance and concentration of conductive species.

[0040] A test concentration (the concentration of the conductive species in the aqueous system at this point in time) is determined, as indicated in steps 314 and 316, by referencing one of the one or more previously determined relationships between cell resistance and concentration of conductive species (sometimes referred to as a calibration curve), and calculating the concentration of conductive species therefrom. The calculation may involve, for example, curve fitting, linear interpolation, or other mathematical modeling techniques.

[0041] In a preferred embodiment, the electrochemical parameters will be such that the test concentration has a numerical value that falls in a range defined by a largest and smallest of the group consisting of all of the concentrations used to establish the relationship described previously. Referring again to FIG. 2, the test concentration preferably falls in a numerical range defined by the largest, B, and the smallest, A, of the group consisting of the first concentration, the second concentration, and any additional concentrations of conductive species that may have been measured to determine the relationship or calibration curve. Using this process, one may "interpolate" within the range of values defined by the calibration curve rather than "extrapolate" beyond the range.

[0042] One may compare the test concentration of conductive species to a predetermined range to determine whether the test concentration is acceptable. For example, if the test concentration is less than a predetermined maximum concentration and greater than a predetermined minimum concentration, one may conclude the concentration is acceptable.

**ELECTROCHEMICAL PLATING**

[0043] The above detailed explanation presents the general case for determining the concentration of conductive species in an aqueous system. One skilled in the art will recognize that this method is applicable to a wide range of

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

industrial and natural systems, products, and processes. The method is particularly advantageous for those applications that employ electroplating cells, with or without an attached power supply. For such applications, it is advantageous to use the electroplating cell in conjunction with embodiments herein to determine the concentration of conductive species in the system.

[0044] Nonlimiting examples of such applications that may advantageously incorporate embodiments herein include the synthesis of various inorganic chemicals, electroless plating, and chemical mechanical planarization.

[0045] FIG. 4 is a cross sectional view of an electroplating process cell 400 that may be used to practice embodiments described herein. The electrochemical cell 102 may be contained in an apparatus for electroplating material layers on a semiconductor wafer or substrate, such as an ELECTRA<sup>TM</sup> plating tool, available from Applied Materials of Santa Clara, California.

[0046] The processing cell 400 generally comprises a head assembly 410, a process kit 420, and an electrolyte collector 440. The electrolyte collector 440 includes an inner wall 446, an outer wall 448, and a bottom 447 connecting the walls. An electrolyte outlet 449 is disposed through the bottom 447 of the electrolyte collector 440, and is connected to the electrolyte replenishing system 220 through tubes, hoses, pipes or other fluid transfer connectors.

[0047] The head assembly 410 generally comprises a wafer holder assembly 450 and a wafer assembly actuator 458. The wafer assembly actuator 458 is mounted onto the mounting plate 460, and includes a head assembly shaft 462 extending downwardly through the mounting plate 460. The lower end of the head assembly shaft 462 is connected to the wafer holder assembly 450 to position the wafer holder assembly 450 in a processing position and in a wafer loading position.

[0048] The wafer holder assembly 450 generally comprises a wafer holder 464 and a cathode contact ring 466. The wafer holder assembly 450 is positioned above the process kit 420. The process kit 420 generally comprises a bowl 430, a container body 472, an anode assembly 474, and a filter 476. Preferably, the anode assembly 474 is disposed below the container body 472, and is attached to a lower portion of the container body 472. The filter 476 is disposed between the

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

anode assembly 474 and the container body 472. The container body 472 is preferably sized and adapted to conform to the wafer plating surface and the shape of a wafer being processed through the system, typically circular or rectangular in shape.

**[0049]** An upper portion of the container body 472 extends radially outwardly to form an annular weir 478. The weir 478 extends over the inner wall 446 of the electrolyte collector 440 and allows the electrolyte to flow into the electrolyte collector 440. The upper surface of the weir 478 preferably matches the lower surface of the cathode contact ring 466. Preferably, the upper surface of the weir 478 includes an inner annular flat portion 480, a middle inclined portion 482 and an outer declined portion 484. When a wafer is positioned in the processing position, the wafer plating surface is positioned above the cylindrical opening of the container body 472, and a gap for electrolyte flow is formed between the lower surface of the cathode contact ring 466 and the upper surface of the weir 478. The lower surface of the cathode contact ring 466 is disposed above the inner flat portion 480 and the middle inclined portion of the weir 478. The outer declined portion 484 is sloped downwardly to facilitate flow of the electrolyte into the electrolyte collector 440.

**[0050]** The anode assembly 474 preferably comprises a consumable anode that serves as a metal source in the electrolyte. Alternatively, the anode assembly 474 comprises a non-consumable anode, and the metal to be electroplated is supplied within the electrolyte from the electrolyte replenishing system 220. As shown in Figure 4, the anode assembly 474 is a self-enclosed module having a porous anode enclosure 494 preferably made of the same metal as the metal to be electroplated, such as copper. Alternatively, the anode enclosure 494 is made of porous materials, such as ceramics or polymeric membranes. A soluble metal 496, such as high purity copper for electro-chemical deposition of copper, is disposed within the anode enclosure 494. The soluble metal 496 preferably comprises metal particles, wires or a perforated sheet. The porous anode enclosure 494 also acts as a filter that keeps the particulates generated by the dissolving metal within the anode enclosure 494. As compared to a non-consumable anode, the consumable (*i.e.*, soluble) anode provides gas-

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS

Express Mail No. EV041916131US

generation-free electrolyte and minimizes the need to constantly replenish the metal in the electrolyte.

**[0051]** An anode electrode contact 498 is inserted into the anode enclosure 494 to provide electrical connection to the soluble metal 496 from a power supply. Preferably, the anode electrode contact 498 is made from a conductive material that is insoluble in the electrolyte, such as titanium, platinum and platinum-coated stainless steel. The anode electrode contact 498 extends through the bowl 430 and is connected to an electrical power supply. Preferably, the anode electrical contact 498 includes a threaded portion 497 for a fastener nut 499 to secure the anode electrical contact 498 to the bowl 430, and a seal 495, such as an elastomer washer, is disposed between the fastener nut 499 and the bowl 430 to prevent leaks from the process kit 420.

**[0052]** FIG. 5 depicts a schematic cross-sectional view of an electrochemical plating cell and device 508. In a preferred embodiment, device 508 applies a cell current to the electrochemical cell 502 and senses a cell voltage that develops across the electrochemical cell 502. In a typical electrochemical plating process, a direct current is applied to the electrochemical cell 502 using device 508. Device 508 generally comprises a power supply 540. Cathode 506 is biased negative in relation to anode 504. Cathode 506 may comprise a semiconductor wafer having a metal layer formed thereon. Cathode 506 may be electrically coupled to, for example, cathode contact ring 466 of FIG. 4. Anode 504 may be electrically coupled to, for example, anode electrical contact 498 in FIG. 4. In operation, electrons combine with a metal cation, such as a copper cation, causing the cation to be reduced on the cathode 506. By this operation, the cation is reduced to a metal, and is thus deposited, or plated, onto the cathode 506. A corresponding oxidation reaction occurs at the anode 504 at which a metallic or conductive species of the anode 504 is converted to a soluble cation that is thereby made available to travel through the electrolyte 500 to the cathode 506.

**[0053]** In an electroplating process, the composition of electrolyte is critical because the composition affects the rate and uniformity of deposition. In particular, the concentration of acid (*i.e.* hydrogen ions) in the electrolyte 500 is

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

maintained at a high enough concentration to prevent variations in process conditions, electrode geometry, or electrode spacing from creating thickness non-uniformities in the plated film. Thus, it is desirable to determine the concentration of acid with an accuracy that is reasonably high.

**[0054]** In general, a direct (DC) current is applied using power supply 540 and a cell voltage is then measured. The cell voltage is measured by device 508. Device 508 may comprise one or more sensing or power supply devices known to the art, such as, for example, a voltmeter 530, to determine cell voltage. Voltmeter 530 may be, for example, coupled in parallel to power supply 540. Power supply 540 may be, for example, a Polara-260 Bipolar Pulsed Supply, commercially available from ENI Corporation of Rochester, NY. Device 508 is typically coupled to a processor and controller, as described in FIG. 1 for device 108. One then calculates the cell resistance of electrochemical cell 102 for a first concentration of acid. The concentration of acid is then adjusted to a second concentration substantially different from the first concentration, and cell resistance is again determined by measuring cell voltage. This process may be repeated for additional concentrations of acid and corresponding measurements of cell voltage are then made. Cell resistance is calculated from cell voltage using the Ohm's law relationship discussed previously. This determines a relationship between the concentration of acid and cell resistance. The relationship may then be used to determine the concentration of acid at any particular point in time for that electrochemical cell 102.

**[0055]** In another embodiment, a relationship between cell resistance and concentration of acid is determined for a plurality of applied cell currents. Referring back to FIG. 3, the process variable of step 309 is cell current. Cell current is adjusted in step 309 and a plurality of relationships between cell resistance and acid concentration for each cell current is then determined.

**[0056]** This embodiment is particularly advantageous in electrochemical plating. The presence of stray capacitance that may exist in a cell, often results in a cell resistance that varies with the cell current. For an electrochemical plating process used in, for example, semiconductor processing, cell current is adjusted periodically to promote uniform plating of a substrate. By generating relationships



**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

between cell resistance and acid concentration for a plurality of cell currents, one is able to determine acid concentration accurately regardless of what cell current is flowing through the electrochemical cell at the time.

**[0057]** For a copper electroplating system such as the one shown, for example, in Figure 4, the cell parameters may be as follows: a copper cathode spaced a distance of about 8 inches from a platinum or copper anode, the anode and cathode having a cross sectional area of about 300 to about 750 square centimeters, and an electroplating bath temperature of about 15 degrees Celsius to about 25 degrees Celsius. Furthermore, the electrolyte may have a concentration of acid of about 3 grams/liter to about 50 grams/liter, and an electrical conductivity between about 40 milisiemens/cm<sup>2</sup> and about 1000 milisiemens/cm<sup>2</sup>. A cell current, *I*, is applied to electrochemical cell 102 and then cell voltage, *V*, that develops across the electrochemical cell 102 is measured. The cell current may, for example, be in the range of about 0.3 Amperes to about 30 Amperes for an aqueous system and electrochemical cell as defined above. The cell voltage may be in the range of about 0.5 volts to about 30 volts.

**[0058]** In a preferred embodiment, the concentration of acid is in the range of about 3 to about 50 grams per liter. The electrolyte typically comprises an acid, such as, for example, sulfuric acid. The electrolyte may further comprise one or more copper salts as well as one or more water-soluble organic molecules known to the art of electroplating.

**[0059]** In another embodiment of the invention, also illustrated in FIG. 1, a system for controlling the concentration of conductive species in an electrolyte 100 is provided. In a preferred embodiment, the system is designed for electroplating a material layer on a semiconductor substrate. The system comprises an electroplating apparatus for electroplating a material layer on a substrate. The electroplating apparatus comprises an electroplating bath comprising an electrolyte 100 with conductive species therein. The system further comprises an electrochemical sensing device 108 capable of continuously measuring one or more electrochemical parameters, such as, for example, cell voltage, of the plating bath.

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

[0060] In addition, the electroplating system further comprises at least one material storage reservoir 120 capable of delivering one or more materials to the electroplating bath in order to adjust the concentration of conductive species therein. The material storage reservoir 120 is coupled to the electroplating bath by mechanical fixtures (not shown) such as valves, etc. to provide control of movement of the materials in the one or more material storage reservoirs 120 to the electroplating bath.

[0061] To facilitate control of the electroplating bath and processes performed therefrom, the system may further comprise a controller 114. The controller may include a processor 118 and other components (not shown). The other components may include memory and support circuits. The processor 118 may be one of any form of computer processor that can be used in an industrial setting for controlling various drives and pressures. The processor 118 may include means for computing specific properties, neural networks or other logic techniques for determining an appropriate flow rate for the one or more chemical components.

[0062] The memory is coupled to the processor 118. The memory or computer-readable medium may be one or more of readily available memory such as random access memory (RAM), read only memory (ROM), floppy disk, hard disk, or any other form of digital storage, local or remote. The support circuits are coupled to the processor 118 for supporting the processor 118 in a conventional manner. These circuits include cache, power supplies, clock circuits, input/output circuitry, subsystems, and the like.

[0063] The controller 114 communicates with mechanical fixtures of the material storage reservoir 120 via a set of connectors 112. The controller 114 communicates information to the mechanical fixtures so as to introduce one or more materials into the electrochemical plating bath to adjust the concentration of conductive species therein. The one or more materials used to adjust concentration of conductive species of the electrochemical plating bath may comprise, for example, an acid, such as sulfuric acid.

[0064] The processor 118 is coupled to the controller 114 via connectors 116. During a plating operation the controller 114 continuously supplies information

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

concerning the concentration of conductive species in electrolyte 100, determined by the electrochemical sensing device 108, to the processor 118. In response, the processor 118 continuously determines an appropriate amount of the one or more materials to be introduced into the electrochemical plating bath from material storage reservoir 120. The amount or concentration of material supplied from material storage reservoir 120 is therefore sufficient to adjust the cell resistance of electrochemical cell 102 so that the concentration is maintained within a predetermined range throughout the plating operation. The processor 118 communicates appropriate information to the controller 114 so as to effectuate an appropriate flow rate for the one or materials in order to introduce an appropriate concentration of the one or more materials in the material storage reservoir 120 into the electrochemical plating bath. Thus, the system provides a real time monitoring of the concentration of material and real time adjustments are made. In a copper plating operation, such as may be used in manufacture of semiconductor wafers, the acidity of the electrochemical bath is the measure of concentration sought.

**[0065]** The processor 118 may be a microprocessor, an ASIC, or some other means for determining desired concentration of conductive species. The system comprising controller 114 and the processor 118 is thus able to function as a self-contained unit, sensing the concentration of conductive species of the electrochemical plating bath and adjusting the electrochemical plating bath by introducing one or more materials in order to effectuate an appropriate concentration of conductive species therein.

**[0066]** In accordance with the disclosure provided, the subject invention is a method for determining the concentration of conductive species in an aqueous medium. The method is advantageous in that it is not labor or time intensive and is relatively inexpensive to operate compared to existing methods. Furthermore, the method is easily adaptable to virtually any aqueous system, and is particularly adaptable to systems such as electrochemical plating and similar operations that utilize an electrochemical cell. The method provides real time monitoring and continuous control of the concentration of conductive species, thereby making it possible to more accurately control the thickness of the plated material.

**PATENT**

Attorney Docket No.: AMAT/5933/CALB/COPPER/PJS  
Express Mail No. EV041916131US

**[0067]** Although various embodiments which incorporate the teachings of the present invention have been shown and described in detail herein, those skilled in the art can readily devise many other varied embodiments that still incorporate these teachings.

2004-01-20 10:40